CHAPTER 11
EMERGING TECHNOLOGIES

CHAPTER CONTENTS

There are several new technologies under development. Some involve substituting solvents coupled with modifications to existing machinery, while others involve the use of newer machinery. The Cleaner Technologies Substitute Assessment (CTSA) briefly describes liquid carbon dioxide (CO_2) and aqueous ultrasonic fabricare technologies and the solvents Rynex and Biotex. There may be others, but these are the only ones USEPA currently has information on. These technologies are in various stages of commercial development, therefore, information is limited and may be speculative.

11.1 LIQUID CARBON DIOXIDE PROCESS

A carbon dioxide (CO_2) process that uses CO_2 in a liquid state is being developed for fabric cleaning. Liquid CO_2 seems to have adequate characteristics for drycleaning garments. Ongoing studies should present a clear determination of the capabilities of drycleaning with liquid CO_2 (Williams et al., Undated). The level of detail on each technology is reflective of its state of development.

Because liquid CO_2 processes are in the pre-commercial stage of development, little information on these processes is available. The information that is available is highly vulnerable to change. Those persons interested in this technology are advised to determine whether more recent information on this technology are available. The following process description summarizes the information available as of December 1997.

Hughes Environmental Systems and Los Alamos National Laboratories (supported by USEPA and the US Department of Energy), have conducted research on this technology, which Global Technologies, Inc. is attempting to commercialize. MiCELL Technologies, Inc. is also developing a liquid CO_2 process (MiCELL, 1997). Although both closed-loop and open-loop liquid CO_2 clothes cleaning were initially investigated (Chao, 1994), pre-commercial machines have been closed-loop. The closed-loop configuration significantly reduces CO_2 emissions by recovering and recycling the solvent in which garments are washed. Because these developing technologies are proprietary, complete process operating parameters are not available.

A problem that is being addressed is how solid materials that are not soluble in liquid CO_2 can be removed from fabric. Liquid CO_2 removes inorganic compounds such as salts even more poorly than PCE. The liquid CO_2 process developers are researching and developing cleaning additives (e.g., detergents) (Caled, 1995; DeSimone and Smith, 1996; and MiCELL, 1997). These cleaning additives may have to be specially formulated for use with liquid CO_2 (Chao, 1994).

The Hughes process was the only process for which process details adequate to describe the unit operations and their configuration were readily available. This pre-commercial Hughes-specific process is described below; if and when a liquid CO_2 process is commercialized, it may differ from that described.

Equipment sizes have not yet been fully determined for the Hughes process, but will probably be similar to those of PCE systems (USEPA, 1996). The following unit operations comprise the Hughes pre-commercial liquid CO_2 process: stationary cylinder, or drum, for washing, extracting, and drying; cooler(s); solvent tanks; a still; filters; a pump; and a compressor. The cleaning cylinder, or drum, is initially charged with about one-half gallon of liquid CO_2 per pound of clothes to be cleaned (Hughes, 1994). In conventional drycleaning, the rotating cylinder provides mechanical agitation of the clothes. In the pre-commercial Hughes-specific liquid CO_2 process, high velocity fluid jets provide mechanical agitation of the clothes during cleaning (Caled, 1995).

The soiled solvent, loaded with both soluble and insoluble (particulate) soils, will circulate in a closed loop, through the cleaning vessel, a filter train, and lint trap, to remove the particulates and lint. At the end of the cleaning cycle, the filtered cleaning fluid is returned to a storage tank. The cylinder will be depressurized, and CO_2 will vaporize from the cleaned clothes. A compressor and condenser will recover much of the CO_2 vapor from the cylinder during depressurization. Some CO_2 vapor loss will occur at the decompression. This loss will require periodic make-up in liquid CO_2 storage. The stored liquid CO_2 will be distilled to remove the soluble soils and detergents. The developer expects the distilling frequency to be similar to that of PCE drycleaning, per unit weight of cleaned garments. To reduce solvent loss, the still "bottoms" (i.e., concentrated mixture of soils and detergents) will be drained without still decompression and stored for recovery and disposal (Caled, 1995).

Global Technologies' DryWash™ cleaning process developmental prototype "Alpha Unit" was displayed during the "Clean '97 Show" in Las Vegas, Nevada. Global Technologies has the right to license seven manufacturers (including Raytheon Commercial Laundry and MVE, Inc.), five chemical additive manufacturers (including Caled Chemical), and one fluid manufacturer (DryWash™ fluid manufacturing corporation headquarters is AGA AB in Stockholm, Sweden) (Global Technologies, 1998). Global Technologies aspires to open test sites and have all its manufacturers in the market in 1998. They estimate that the capital production price of machines with DryWash™ will be $80,000 (Kinsman, 1998). Cycle times for these machines will be 30 minutes.

MiCell Technologies expects the MiCARE process to be available in 1998 (USEPA, undated). The estimated commercial price for their MiCare™ machine is approximately $150,000 (Lienhart, 1998).

The NIOSH Criteria Document for CO_2 provides the following hazard information (SRI, 1976). A large body of human experimental information suggests the potential for CO_2 exposure to cause respiratory, cardiovascular, central nervous system, behavioral, electrolyte balance, and muscle effects over a variety of concentrations and durations. Inhalation of carbon dioxide at concentrations greater than 17% is lethal to humans.

No irritation or sensitization studies were reported in the literature discussed by NIOSH. Continuous exposure to 1.5–3% CO_2 (15,000 to 30,000 ppm in air) does not result in serious toxicity to humans. Physiological effects at these exposure levels include increased CO_2 and bicarbonate ion levels in blood, changes in other electrolyte levels, and increased ventilation rates.

Two weeks of exposure to 4% CO_2 in an environmental chamber showed no psychomotor impairment and no decrement in complex-task performance by six healthy male human subjects. Exposure of an unspecified number of men to 3% CO_2 for 8 days, however, showed a progression through mental stimulation and euphoria at day 1 to exhaustion and confusion on days 2 through 8. NIOSH does not summarize any human studies focusing on reproductive and/or developmental toxicity, although some studies in laboratory animals have shown these effects at very high doses.

No mutagenicity studies are summarized by NIOSH. There were no reports of carcinogenicity in animals or in humans from inhalation of gaseous CO_2.

Williams et al. (undated) conducted a study using liquid CO_2 in both small-scale and pilot-scale test systems to address fabric compatibility with this alternative cleaning method, compared with drycleaning using PCE. The study concluded that the liquid CO_2 technology is not necessarily a “drop-in” replacement for PCE drycleaning, although liquid CO_2 is an effective solvent for removal of common types of organic soils. Researchers noted that liquid CO_2 processing had no deleterious effects on test fabrics, had acceptable shrinkage, and removed more soil than standard PCE drycleaning. The next step, according to the study, would be to evaluate full scale prototype cleaning units, which are currently under development.

11.2 ULTRASONIC CLEANING PROCESS

Aqueous-based ultrasonic washing processes have been used in industrial cleaning applications for many years. It is now being researched for garment cleaning. Ultrasonic cleaning uses high intensity sound waves in a fluid medium to create mechanical forces that dissolve and displace contaminants on clothing. No ultrasonic process equipment description is available. This section discusses several of the concepts and issues involved in the development of this process.

Surfactants, detergents and/or ozone may theoretically be used in an ultrasonically agitated aqueous solution to clean stationary garments. Free-floating items tend to severely dampen ultrasonic energy in solutions, and this dampening would not allow for needed mechanical agitation. Transducers create cavitation, which may dislodge insoluble particles from the garments in the cleaning solution. A combination of blended detergents and ultrasonics may allow polar and non-polar contaminants to be removed at temperatures between 90°F to 122°F (32°C to 50°C) without fabric damage (Abt, 1994). If developed, a machine that could accomplish such cleaning would achieve similar results to the washer in the machine wetcleaning system. Extraction and drying would need to be incorporated into this ultrasonic system.

Cavitation creates the mechanical agitation in ultrasonic cleaning. Cavitation is energy created by the conversion of electrical pulses to acoustic energy via transducers which are bottom- or side-mounted in the cleaning system. This energy exists in the cleaning solution as alternative rarefactions and compressions of the liquid. During the rarefaction, small vacuum cavities are formed that collapse or implode during compression. This continuing process, called cavitation, is responsible for the scrubbing effect that dislodges contaminating particles (Abt, 1994). According to one source who has conducted small-scale research in ultrasonic cleaning, three areas of change must be researched for this process:

- Optimizing the time and temperature of washing, the ultrasonic agitation, and the detergents needed to provide adequate cleaning;
- Designing systems for rinsing, dewatering, and drying; and

- Designing a material handling system (Porter et al., 1995).

Proponents of ultrasonic cleaning claim that it is faster, uses less water and energy, and performs more thorough cleaning than conventional fabricare cleaning methods (Hoffman, 1998). The Department of Energy provided funding for a test of ultrasonic cleaning in 1993. Since that time, further work has been conducted at North Carolina State University using continuous processing. Currently, the Fraunhofer Technology Center, a joint venture of the City of Hialeah, Florida and Fraunhofer USA, is raising funds to develop a prototype ultrasonic clothes cleaning machine.

11.3 RYNEX SOLVENT

Rynex Corporation currently is developing a drycleaning solvent named Rynex for substitution in existing PCE machines. This solvent is a mixture containing one or more propylene glycol ethers. The following process information summary contains the information available as of December 1997, with the exception of a personal contact from April 1998.

Rynex Corporation intends this solvent to be a drop-in substitute for PCE in modified PCE machinery. The company claims that PCE drycleaners could use this mixture by modifying cycle times and temperatures, installing a new water separator, and cleaning the PCE from the machinery, and filling the machine with the mixture (Colletti, 1998). A water separator change would apparently be necessary because the Rynex mixture has a lower density than water (Rynex, 1997). The Rynex mixture would then be removed from the top of the separator, and water would be removed from the bottom. The Rynex mixture and water phase separation would be opposite to that of PCE and water because PCE has a higher density than water. In the PCE separator, PCE is removed from the bottom of the separator, and water is removed from the top.

Rynex is currently being studied in five test sites. Although official performance reports have not yet been released, the company claims that the chemical has the following advantageous characteristics: biodegradablity, contains no hazardous materials or carcinogens, recyclable via distillation, and a flashpoint higher than HC solvents (Colletti, 1998).

Rynex is considered a volatile organic compound (VOC), its use by cleaners may be regulated by state and Federal air pollution legislation. However, Rynex is not regulated as a hazardous air pollutant (HAP) under the Clean Air Act (Hayday, 1998).

Hazard data are available for a variety of propylene glycol ethers. Proprietary information precludes identification of the particular solvent used in Rynex, but it is known to be a propylene glycol ether. USEPA has published a review of the hazard information on several propylene glycol ethers (USEPA, 1986), however, and also recently derived a reference concentration (RfC) on a specific propylene glycol ether, propylene glycol monomethyl ether (PGME) (IRIS, 1998).

Propylene glycol ethers appear to be extensively absorbed following either oral or inhalation exposure. There is no information on absorption following contact with the skin. A study with a small number of human volunteers exposed to moderate levels of PGME in air resulted in eye, nose, and throat irritation and headaches, but there were no controls in the study.

In animal studies, exposure (via drinking water, oral intubation, or inhalation) to high concentrations of PGME resulted in general toxicity (lowered body weights) and specific effects on the liver and the central nervous system (narcosis/sedation effects).

Limited studies in animals suggest no developmental or reproductive effects following exposure to several different propylene glycol ethers. No studies reviewed in either USEPA document were designed to examine whether these chemicals interact with genetic material or cause cancer.

11.4 BIOTEX SOLVENT

Another new cleaning process still in development is based on a new solvent, tentatively named "Biotex," by the developer Bio-Clean Ventures. In a May 27, 1998 communication to USEPA, Dieter Berndt, PhD, Director of R&D for Bio-Clean indicates their plans to market "Biotex" as an alternative to PCE and HC solvents. The company claims "Biotex" is non-carcinogenic, not a VOC, its use will not result in the production of secondary hazardous waste, and that its distillation residue will be dischargeable into ordinary sewage (Berndt, 1998) although these claims are unsubstantiated by USEPA.

Bio-Clean Ventures states that "Biotex" will be "...a little higher [priced] than Perc" and makes the following claims, based on their "extensive" testing program:

- Drycleaners will be able to use "Biotex" in existing PCE machines, with certain modifications to their equipment;
- "Biotex" can also be used in existing HC machinery without modification.;
- The solvent will not attack or pull dyes of any type, even at temperatures over 150°F, nor will it shrink garments;
- It has a degreasing ability of around 58-63, as compared to PCE at 90 and HC at 31;
- It has a surface tension of 16 dynes/square cm, as compared to PCE at 36; and
- It is slightly lighter than water.

No studies have been found to verify these claims, and the commercial status of this solvent is currently unknown.

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